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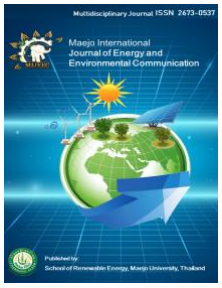

ARTICLE

Lignocellulosic valorization of groundnut shells for bioethanol: Energy potential and techno-economic feasibility

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ABSTRACT

This study investigates optimized calcium oxide (CaO) alkaline pretreatment to create sustainable bioethanol production from groundnut shell waste while evaluating its physical and chemical properties alongside bioenergy capabilities. The versatile properties of groundnut shells obtained from agricultural residues include low moisture content (9.5% wet basis), together with high volatile matter (70.2%) as well as fixed carbon (18.1%), while maintaining low ash content (3.2%) which makes these shells suitable for thermal and biochemical conversions. Their lignocellulosic composition 32.8% cellulose, 20.1% hemicellulose, and 27.4% lignin. CaO pretreatment at 2% w/v concentration led to improved biomass digestibility, which produced total sugars at 465.2 mg/g and reducing sugars at 297.4 mg/g from the material. Enzymatic hydrolysis of the pretreated biomass achieved an additional glucose concentration of 318.7 mg/g. When *Saccharomyces cerevisiae* fermented the hydrolysate for 120 hours, it produced 33.6 g/L of ethanol, representing 88% theoretical yield. The pretreatment and subsequent hydrolysis stages yielded reducing sugar recovery rates of 86.5% and 84.1%, respectively, and total sugar recovery rates of 91.6% and 88.3%. Groundnut shells provide a substantial promise as a renewable energy resource because they have a 17.2 MJ/kg heating value and 13.9 MJ energy potential per kilogram of dry biomass. The integrated approach demonstrates the technical viability of bioethanol production from groundnut shells while contributing to sustainable agricultural practices and waste management, and operating within low-carbon energy systems of the circular bioeconomy framework.

1. Introduction

A low-carbon sustainable energy future stands as a worldwide critical priority because of international agreements like the Paris Agreement, together with the European Green Deal and national objectives for mid-century net-zero greenhouse gas (GHG) emission targets (Asif et al., 2024). A major transformation of the energy sector needs to occur to reduce global emissions, since the sector produces approximately three-quarters of these emissions, using renewable energy technologies and efficiency measures, and eliminating fossil fuels as sources of energy (Gotore et al., 2024; Onyemowo et al., 2024). The decarbonization of hard-to-decarbonize areas like transportation and agriculture, along with rural energy systems, depends heavily on bioenergy with liquid biofuels, including bioethanol, that serves as a renewable carbon-reducing alternative (Nasution et al., 2024). Bioethanol functions as an established component in worldwide fuel blends because the United States, Brazil, and the European Union are

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leaders in production. The heavy usage of first-generation bioethanol from plant-derived starch and sugar crops like corn and sugarcane presents problems that affect food security and lead to indirect land use changes alongside environmental impacts (Taechawatchananont et al., 2024). The combination of an expanding global population along with unstable food markets, and agricultural disruptions caused by climate change has led to increased challenges. The scientific world, together with policy authorities, now concentrates its efforts on second-generation (2G) bioethanol production through non-food sources of lignocellulosic biomass comprising agricultural residues and forestry waste, and industrial by-products because these alternative feedstocks deliver more sustainable fuel opportunities (Manmai et al., 2020; Trejo et al., 2023).

The Earth holds a vast quantity of organic biomass resources, with lignocellulosic materials being the major group, consisting of cellulose and hemicellulose, and lignin components (Dussadee et al., 2022). Groundnut (peanut) shells rank among the leading underutilized agro-residues because of their extensive volume. The annual global production of groundnuts reaches 47 million tons, which generates more than 8 million tons of shell waste annually because there are between 20–30% residues remaining from this biomass (Ezejiofor et al., 2014). Groundnut shells show high prevalence as disposal materials through landfilling, together with incineration and discarding processes, which lead to environmental risks, emission of carbon, and elimination of valuable resources (Duc et al., 2019). However, their composition—high cellulose (30–35%), moderate hemicellulose (18–22%), low ash content (~3%), and calorific value (~17–18 MJ/kg)—makes them a promising feedstock for biochemical conversion into ethanol and other value-added bioproducts. Complex technical issues exist in the biomass conversion process because the plant cell wall shows both structural rigidity and chemical resistance. The heterogeneous polyphenolic polymer lignin develops into a protective sheath that hinders enzyme access to both cellulose and hemicellulose. Efficient pretreatment remains crucial for 2G bioethanol production, requiring methods that break lignin-carbohydrate complexes while preserving sugar content and preventing inhibitors (Manmai et al., 2020).

A promising, less expensive strategy for lignocellulosic material delignification exists through the use of calcium oxide (CaO) based alkaline pretreatment (Sophanodorn et al., 2022a). During the reaction between CaO and lignin, the substance produces calcium-lignate complexes that enable separation and removal while creating more accessible cellulose (Chen et al., 2022). The use of CaO in pretreatment reduces environmental impact and improves operability of bioethanol systems run by decentralized rural facilities (Manmai et al., 2020). Studies have confirmed that wheat straw and bagasse pretreatment with 2-3% w/v CaO allows the removal of 60% of lignin while improving enzymatic digestibility by more than 2.5 times. The accessible cellulose and hemicellulose within the pretreated material transform into monomeric sugar molecules through biochemical hydrolysis, which results mainly in glucose and xylose. The enzymatic hydrolysis requires cellulase enzymes that contain endoglucanase and exoglucanase functions, together with β-glucosidase enzymes, along with optional hemicellulase supplements to process arabinoxylans and other branched materials (Zhang et al., 2020). The hydrolysis process depends on various operational parameters, which include enzyme load, residence time, and pH value of 4.8–5.0, and temperature at 50–55°C, alongside the pretreatment extent of biomass. Commercial systems reaching maximum theoretical sugar outputs from 70% to 90% require further development for cost-effective industrial scale-up operations.

The industrial yeast species *Saccharomyces cerevisiae* performs fermentative sugar conversion into ethanol as its main function in biotechnology. The yeast strain *S. cerevisiae* demonstrates excellent performance regarding ethanol productivity, together with osmotolerance and robust process operation (Kongchan et al., 2022; Mejica et al., 2022). Natural fermentation of the pentose sugar xylose cannot occur in lignocellulosic hydrolysate because this fermentable sugar makes up 10–30% of hemicellulose-rich biomass sugars. The limit of microbial fermentation is now resolved via metabolic engineering and synthetic biology approaches that produce recombinant strains that can process xylose together with glucose to boost total ethanol output efficiency. Each kilogram of groundnut shells processed leads to a 270–300 milliliter ethanol production, which equates to 13.9 MJ usable energy based on the ethanol heating value of 26.8 MJ/kg. Available data indicates that biomass energy conversion reaches 70–80% of its original form, which stands as a favorable result against various bioenergy systems. The GHG emission reductions from ethanol production through lignocellulosic waste reach 85–90% compared to gasoline when renewable energy sources and biogas from lignin-rich residues power the process (Igwebuike et al., 2024).

The sustainable management of groundnut shells through development prevents the emission of methane and black carbon, and particulate matter (PM2.5) from open fires and uncontrolled decomposition processes. The process converts wasted materials into renewable energy and valuable digestate byproducts suitable for use as organic agricultural fertilizer (Khaodee & Chaiworn, 2023). From an economic standpoint, Second-generation ethanol requires additional capital expenditure for pretreatment reactors along with enzyme tanks and solid handling units, yet its operation costs decrease substantially through using free waste materials (Sophanodorn et al., 2022), such as groundnut shells. The minimum ethanol selling price for lignocellulosic systems ranges between USD 0.90–1.20/L and stands higher than the USD 0.50–0.70/L price range of first-generation ethanol (Aui et al., 2021). The combination of improved enzyme efficiency and scale-up integration strategies, and carbon credit monetization mechanisms will enable 2G ethanol to achieve cost parity during the following ten years. Small-scale biorefineries operating in a decentralized manner across agricultural areas generate several advantages. This research investigates the practicality of obtaining bioethanol from groundnut shell biomass by performing a comprehensive analysis of physicochemical assessments and CaO-based alkaline pretreatment, and enzymatic hydrolysis and fermentation procedures. This study advances circular bioeconomy principles while supporting biomass-derived fuel roles during the carbon neutrality transition by leveraging an abundant groundnut shell resource base.

2. Materials and Methods

Figure 1 illustrates the details of all the required steps for creating second-generation bioethanol from groundnut shell waste. The first steps include biomass collection along with cleaning, followed by drying and milling before sieving the material, while compositional analysis is conducted to determine lignocellulosic content. The combination of CaO-based alkaline treatment improves cellulose availability so that enzymes can break down fermentable sugar

compounds. *Saccharomyces cerevisiae* carries out ethanol fermentation of these sugars. The process is evaluated based on energy yield and economic viability as well as environmental sustainability, to guarantee efficiency and ecological friendliness.

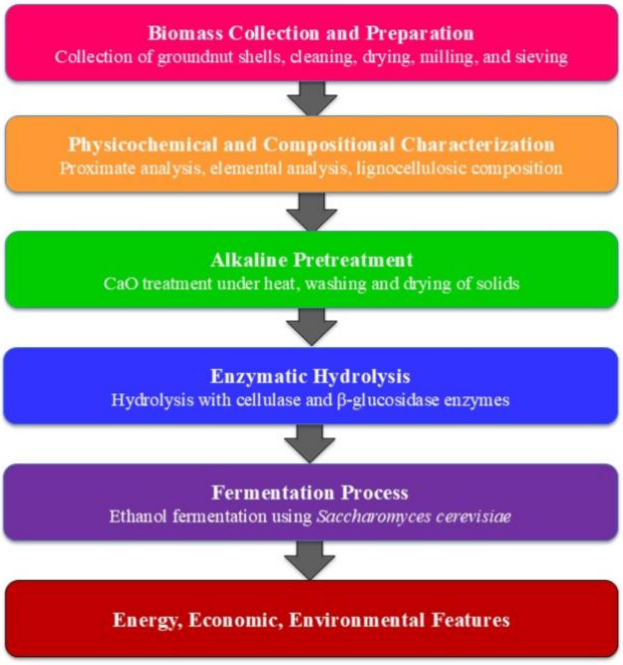


Figure 1. Conceptual diagram of bioethanol production from groundnut shells

2.1 Biomass collection and preparation

Groundnut shells were collected from a local oil extraction and processing facility located in the suburban zone of Pune, India. The raw shells were manually separated from impurities such as soil, stones, and broken pods. The biomass was then sun-dried for 48 hours to reduce surface moisture, followed by oven drying at 60°C for 24 hours to achieve a constant weight (moisture content <10%). Dried shells were milled using a hammer mill and sieved to a uniform particle size of 0.5–1.0 mm using ASTM mesh screens to ensure homogeneity prior to pretreatment and compositional analysis.

2.2 Physicochemical and compositional characterization

The laboratory performed proximate analysis through ASTM standards E871, E872, and D1102 to measure moisture and volatile matter, along with ash, as well as fixed carbon contents (Özsin et al., 2019). A CHNS elemental analyzer model PerkinElmer CHNS-O (or equivalent) determined the carbon, hydrogen, nitrogen, and sulfur concentrations through ultimate analysis (Van Soest et al., 1991). The analysis of lignocellulosic composition proceeded through the modified Van Soest detergent fiber method for NDF/ADF/ADL determination (Gaur & Reed, 1995). The fractions of cellulose and hemicellulose and lignin were determined through three steps in this analysis:

Hemicellulose = NDF – ADF

Cellulose = ADF – ADL

Lignin = ADL

The measurements were carried out in three independent trials, and they reported results as average values with standard deviation measurements. The higher heating value (HHV) measurement of biomass took place within a bomb calorimeter (IKA C2000 Basic), which operated under adiabatic conditions (ASTM 2010).

2.3. Alkaline pretreatment with calcium oxide (CaO)

Pretreatment was carried out using analytical-grade calcium oxide (CaO, ≥95% purity). Dried groundnut shell powder (20 g) was mixed with 500 mL of aqueous CaO solution at concentrations ranging from 0% to 4% (w/v). The mixtures were subjected to thermal treatment at 90°C in a sealed, stirred reactor for 2 hours (Yu et al., 2010). After cooling, the slurry was filtered using vacuum filtration through Whatman No. 1 filter paper, and the solids were thoroughly washed with distilled water until a neutral pH was reached to remove residual $Ca(OH)_2$ and lignin complexes. The washed solids were oven-dried at 60°C for 24 hours and stored in airtight containers for further enzymatic hydrolysis. Samples from each pretreatment condition were analyzed to assess lignin removal and structural changes via compositional re-analysis.

2.4. Enzymatic hydrolysis

Enzymatic hydrolysis was performed using a commercial cellulase preparation (e.g., Celluclast® 1.5L, Novozymes) with an activity of 700–1000 U/g, supplemented with β-glucosidase (e.g., Novozyme 188). Pretreated biomass (5 g dry weight) was suspended in 100 mL of 50 mM citrate buffer (pH 4.8) in 250 mL Erlenmeyer flasks. Hydrolysis was conducted at 50°C for 48 hours in a shaking incubator set at 150 rpm. Enzyme loadings were varied between 0% and 3% (v/v) based on optimization trials. Samples were periodically withdrawn and centrifuged at 10,000 rpm for 10 minutes. The supernatant was analyzed for total sugars (phenol-sulfuric acid method) and reducing sugars (DNS method) (Dubois et al., 1956; Miller, 1959), with glucose quantification confirmed via high-performance liquid chromatography (HPLC) equipped with a refractive index detector and an Aminex HPX-87H column.

2.5. Fermentation process

Hydrolysates generated from the 2.0% cellulase-treated biomass were used for ethanol fermentation. Prior to inoculation, hydrolysates were adjusted to pH 5.0 and sterilized at 121°C for 15 minutes. *Saccharomyces cerevisiae* (ATCC 9763) was used as the fermentative organism (Taherzadeh & Karimi, 2008). The yeast was activated in yeast peptone dextrose (YPD) medium and inoculated at 10% v/v into 100 mL of hydrolysate in 250 mL anaerobic serum bottles equipped with fermentation locks. Fermentation was carried out at 30°C for 120 hours under static conditions. Samples were collected at 24-hour intervals and centrifuged. The supernatant was analyzed for ethanol content using gas chromatography (GC-FID) with an ethanol standard calibration curve (Alvira et al., 2010). Residual sugars were monitored by HPLC to assess sugar consumption. Fermentation parameters such as ethanol yield (g/g sugar), productivity (g/L/h), and sugar utilization efficiency (%) were calculated.

2.6. Analytical Techniques

Sugar quantification was performed using standard colorimetric assays, specifically the DNS method for reducing sugars and the phenol-sulfuric acid method for total sugars (Dubois et al., 1956; Miller, 1959), with results validated by high-performance liquid chromatography (HPLC) equipped with a refractive index detector (Shimadzu, RID-10A). Ethanol concentration in the fermentation broth was determined using gas chromatography with a flame ionization detector (GC-FID; Agilent 7890B) and a DB-FFAP capillary column (Taherzadeh & Karimi, 2008). Lignin removal efficiency was assessed by comparing acid detergent lignin (ADL) values before and after alkaline pretreatment. Enzymatic hydrolysis efficiency was calculated as the percentage of glucose released relative to the theoretical maximum based on the initial cellulose content. All experimental measurements were conducted in triplicate, and results are reported as mean values with corresponding standard deviations.

2.7. Energy balance and yield calculation

Energy output from bioethanol was calculated based on the ethanol yield and its lower heating value (LHV = 26.8 MJ/kg). Energy conversion efficiency (%) was calculated as:

$$\text{Efficiency}=\left(\frac{Energy\ in\ Ethanol}{HHV\ of\ Biomass\ Input}\right) x\ 100$$

2.8. Techno-economic analysis

A preliminary techno-economic assessment (TEA) was conducted to evaluate the feasibility of ethanol production from groundnut shells under a decentralized rural biorefinery model. Capital costs, enzyme and nutrient inputs, energy requirements, and yield outputs were used to estimate the minimum ethanol selling price (MESP). Cost inputs were sourced from literature benchmarks and adjusted to reflect regional values (Balan, 2014); Humbird et al., 2011). Sensitivity analysis was performed by varying enzyme costs, feedstock availability, and fermentation time. Environmental co-benefits, including GHG reduction and waste diversion potential, were qualitatively evaluated based on existing life cycle assessment (LCA) data for similar feedstocks (Gnansounou, 2010).

3. Results and Discussion

3.1 Physicochemical characterization of groundnut shells

Groundnut shells, also known as peanut shells, are a lignocellulosic agricultural residue characterized by a composition rich in cellulose, hemicellulose, and lignin (Table 1). On a dry weight basis, these shells typically comprise approximately 30–40% cellulose, 15–20% hemicellulose, and 25–35% lignin, along with a minor fraction of ash. For instance, one study reported that groundnut shells contain approximately 35.7% cellulose, 18.7% hemicellulose, 30.2% lignin, and about 5.9% ash. In certain instances, the cellulose content may be even higher (around 45%), while hemicellulose is lower (approximately 6%), with lignin constituting about 36%. This variability is influenced by factors such as cultivar and growing conditions. Regarding proximate analysis, groundnut shells exhibit a moderate moisture content when air-dried, typically ranging from approximately 6–11%. Their volatile matter content is high, generally constituting 68–80% of dry weight, whereas fixed carbon is relatively low for a solid fuel, often around 15–22%. For example, Yahya et al. (2023) found that groundnut shell samples contained about 68.2% volatile matter (the lowest among several biomasses tested) and 22.3% fixed carbon (the highest among those biomasses). The ash content of groundnut shells is low, often only about 1–3% in raw form, which is advantageous as it results in fewer inorganic residues and reduces the risk of mineral inhibitors during processing. The shells also possess a significantly higher heating value (HHV), ranging from 15–22 MJ/kg. Indeed, one characterization study reported an HHV of approximately 22.18 MJ/kg for groundnut shells, which is higher than values reported by earlier researchers (approximately 15–19 MJ/kg range). This high energy content correlates with the shells' high fixed carbon and lignin content, rendering them a potential energy source for cogeneration.

Table 1. Physicochemical properties of groundnut shells

Property	Value ± SD
Moisture content (wet basis)	9.5 ± 0.3%
Volatile matter	70.2 ± 2.1%
Fixed carbon	18.1 ± 1.2%
Ash content	3.2 ± 0.9%
Cellulose	32.8 ± 1.5%
Hemicellulose	20.1 ± 1.1%
Lignin	27.4 ± 1.4%
Higher Heating Value (HHV)	17.2 ± 0.4 MJ/kg
Bulk Density	210 ± 12 kg/m³

Nevertheless, a challenge associated with groundnut shell feedstock is its bulk density. The loose shells exhibit very low density, approximately 0.1–0.25 g/cm/m³ (e.g., roughly 100–250 kg/m³) in raw form, which implies they occupy a large volume for a given mass. For example, in an Indian biomass survey, the bulk density of loose groundnut shells was about 255 kg/m³, whereas densified briquettes made from the shells had a density of approximately 680 kg/m³. This low bulk density impacts transportation and handling, a consideration for bioethanol supply chains, often mitigated by grinding or pelletizing the shells prior to processing. The compositional analysis of raw groundnut shells revealed a moisture content of 9.5 ± 0.3% (wet basis), volatile matter of 70.2 ± 2.1%, fixed carbon of 18.1 ± 1.2%, and ash content of 3.2 ± 0.9%, indicating their suitability for thermochemical and biochemical conversion processes. Lignocellulosic composition showed cellulose at 32.8 ± 1.5%, hemicellulose at 20.1 ± 1.1%, and lignin at 27.4 ± 1.4%. These values are consistent with previous studies on peanut shell biomass, confirming their high carbohydrate content. The HHV was measured at 17.2 ± 0.4 MJ/kg, suggesting a favorable energy density for downstream processing. The overall composition supports their classification as a viable lignocellulosic feedstock for second-generation bioethanol production.

3.2 Effect of CaO pretreatment on sugar release

The amounts of fermentable sugars extracted from groundnut shells increased significantly following CaO pretreatment, while reaching an optimum concentration level shown in Figure 2. The enzymatic hydrolysis produced minimum amounts of total sugars and reducing sugars, and glucose during hydrolysis when no CaO (0% w/v) was present. The increase of CaO concentration from 1% to 3% caused a significant improvement in all sugar yield measures. Total sugar production at 3% CaO reached its highest level, which exceeded multiple times the sugar yield of the control without treatment. All

three sugar and glucose yields achieved their maximum values at 3% CaO concentration. The addition of CaO causes delignification, so biomass structure disruption takes effect as it removes lignin when used as a mild alkali to boost enzyme access toward cellulose and hemicellulose (Premjet et al., 2025). The pretreatment with 3% CaO reached an ideal state of lignin removal, which maximized sugar yields because it achieved optimal delignification. The addition of CaO beyond 3% did not enhance sugar production because the 3% concentration yielded better results than the 4% concentration. The excessive alkaline conditions at the highest CaO loading appear to interfere with sugar production since high alkalinity may damage available sugars (Manmai et al., 2023).

Experimental results show that the reduction of performance after the optimal CaO concentration emerges from over-treatment processes. The use of elevated amounts of alkali no longer enhances lignin removal, yet leads to carbohydrate losses because of peeling or degradation reactions (Sophanodorn et al., 2022b). The process of additional base addition after most lignin removal leads to cellulose/hemicellulose degradation and converts them into byproducts, which cannot contribute to sugar yields (Shukla et al., 2023). The sugar yields decrease slightly when the CaO dosage reaches 4%. The same results have been reported in investigations of alkaline pretreatment methods. The pretreatment of broom grass with moderate sodium hydroxide concentrations reached maximum efficacy at 2% w/v according to Premjet et al. (2025), as they achieved 74.7% lignin removal with 93% glucan recovery, while further increasing NaOH resulted in no additional benefits. The maximum biogas (also known as methane) production from the enzymatic processing of groundnut shells occurred when researchers applied an intermediate base concentration, according to Olatunji & Madyira (2024), but increased alkalinity levels diminished biogas output. The research shows that severe alkaline conditions lead to negative effects, which matches the experimental observations from the 4% CaO over-treatment condition.

The highest sugar outputs occurred due to the pretreatment with 3% w/v CaO because it achieved maximum delignification with superior carbohydrate retention. The optimized delignification stage at this point enhanced enzymatic hydrolysis operations as demonstrated by higher levels of reducing sugars and glucose obtained. A minor decrease in pretreatment severity from 3% w/v to 4% suggests that any additional pretreatment would offer no further benefits. Our research outcome shows consistency with the reported concept that alkaline pretreatment technologies should be adjusted specifically for each raw material to achieve optimal recovery of sugars with minimal degradation (Shukla et al., 2023). The use of CaO pretreatment with lime successfully produced similar outcomes for biomass-to-ethanol studies as demonstrated by Chen et al. (2024), who achieved over 90% cellulose conversion rates in lime-treated corn stover, directly affecting both sugar production and ethanol yields.

CaO establishes itself as an effective pretreatment agent since its optimal implementation conditions produce high conversion efficiencies (Sophanodorn et al., 2022c). The study, together with recent literature, reveals that sugar yields decrease from excessive CaO pretreatment beyond optimal conditions (Shukla et al., 2023). The use of increasing CaO up to its optimal level produces better sugar yields from groundnut shells by enhancing delignification, but using concentrations above this point does not lead to additional benefits. The maximal sugar yields at 3% CaO represent a pretreatment level that provides effective delignification for obtaining the best enzymatic sugar results. A sugar yield reduction occurred using 4% CaO because additional CaO interaction might have led to minimal cellulose/hemicellulose damage as well as inhibitor generation. The research outcomes align with present studies demonstrating that median alkaline pretreatment methods lead to enhanced digestibility, yet excessive conditions result in a reduction of fermentable sugar yield (Vu et al., 2018). Our research demonstrates that CaO pretreatment intensity is directly linked to sugar production rates while showing that excessive treatment quality gives rise to suboptimal results for bioethanol generation, as established in both our studies and modern research findings.

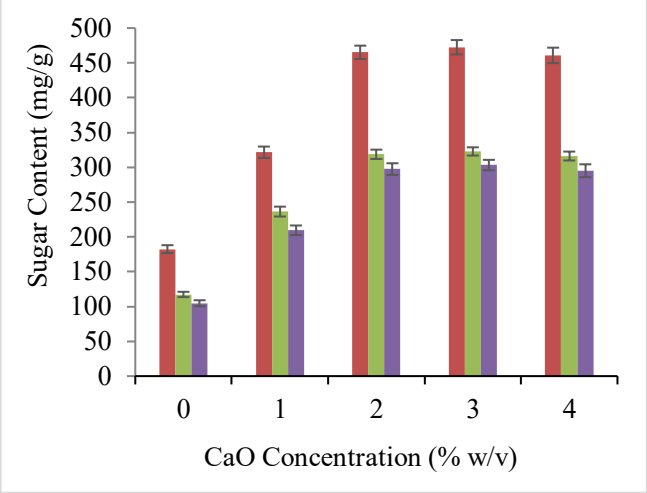


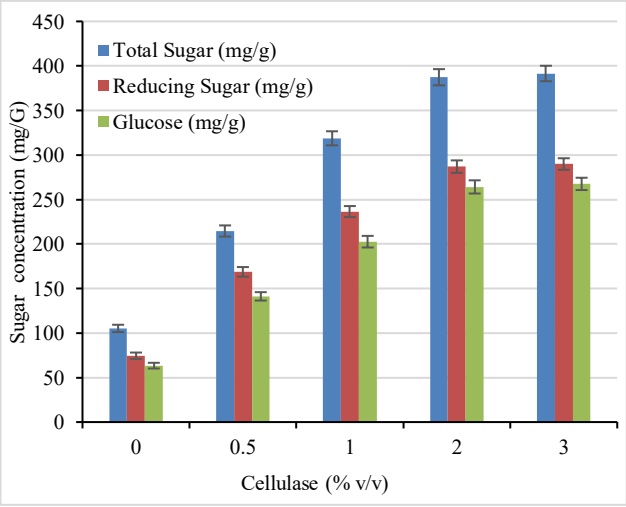
Figure 2. Sugar yields from pretreated groundnut shells (0% to 4% w/v CaO alkaline pretreatment)

3.3 Effect of enzymatic hydrolysis on sugar yields: Optimization of cellulase loading

The enzymatic hydrolysis process functions as an essential step for converting pretreated biomass polysaccharides into monosaccharides suitable for fermentation. Figure 3 shows that pretreated groundnut shells produced a substantial increase of sugar during hydrolysis when cellulase v/v concentration was increased from 0 to 3%. The results demonstrate standard enzymatic hydrolysis behavior because additional enzymes lead to higher sugar yields at optimal concentrations before reaching maximum production limits (Nwamba et al., 2021). The low levels of total sugar release (105.2 ± 4.1 mg/g) at 0% cellulase definitively show pretreatment methods fail to release fundamental amounts of fermentable sugars from lignocellulose. The results from this initial condition clearly demonstrate the critical importance of enzymatic catalysis to saccharify the cellulose and hemicellulose components (Sawargaonkar et al., 2024).

The addition of 0.5% cellulase led to a doubling of sugar yields up to 214.6 ± 6.3 mg/g total sugars and 168.7 ± 5.4 mg/g reducing sugars. The data shows that low amounts of cellulase enzymes successfully target exposed cellulose fibers after CaO pretreatment because this treatment breaks down barriers made of lignin (Sophanodorn et al., 2022a). The utilization of increased enzyme amounts resulted in continuously growing sugar outputs. The solution containing 1.0% and 2.0% cellulase produced sugar release levels of 318.7 ± 7.9 mg/g and

387.3 ± 9.1 mg/g, respectively. The concentrations of glucose rose alongside other sugar products, which demonstrated efficient transformation of cellulose into fermentable monosaccharides. The 2.0% cellulase treatment achieved major success as it produced 286.9 ± 7.0 mg/g of reducing sugars along with 264.1 ± 7.4 mg/g of glucose to establish itself as the most effective enzyme concentration for sugar maximization while reducing excess enzyme consumption. The total sugars reached 391.5 ± 8.7 mg/g, and glucose amounted to 267.5 ± 6.9 mg/g using 3.0% cellulase concentration because enzyme saturation conditions have been met. The observed saturation point in sugar yields follows the documented approach of saturation kinetics because additional enzyme concentration does not bring significant product increases (Premjet et al., 2025). The remaining cellulose has two potential barriers preventing enzymatic breakage: crystalline structures



or encapsulating lignin residues (Shuai et al., 2016).

Figure 3. Sugar yields from pretreated groundnut shells using enzyme hydrolysis (0% to 3% v/v cellulase)

The study findings support data obtained through the latest enzymatic hydrolysis experiments with lignocellulosic biomass. The research conducted by Shukla et al. (2023) showed that the utilization rates of cellulase enzymes for sugarcane bagasse and rice straw processing reached optimum levels between 1–2% v/v, while further enzyme additions ceased to yield proportionate sugar results due to substrate saturation effects and non-productive enzyme binding mechanisms. Shuai et al. (2024) showed that after pretreating peanut shells through the γ-valerolactone process and adding enzyme at a rate of 20 FPU/g the glucose yield reached a significant level but further performance plateaued. Financial considerations regarding enzymes play a vital role during production expansion. The analysis indicates that utilizing 2.0% v/v cellulase represents the most profitable option for bioethanol producers since additional enzyme addition between 2.0% and 3.0% leads to negligible yield improvements but increases production expenses by 30–50%. Enzyme recycling along with synergistic co-enzyme supplementation (such as xylanase and β-glucosidase) tend to achieve better efficiency than simply raising the cellulase amount (Nwamba et al., 2021). The maximum sugar yield during enzymatic hydrolysis of pretreated groundnut shells was achieved when using approximately 2.0% v/v cellulase concentration. The enzyme-substrate interaction shows its behavior through minimal improvements at dosages above the dosage point (Ramaraj & Unpaprom, 2019). The study backs existing scientific research by demonstrating that enzyme optimization plays a critical role in developing viable and efficient processes for bioethanol production from lignocellulose.

3.4 Fermentation kinetics of groundnut shell hydrolysate: Ethanol yield and sugar utilization efficiency

Description of fermentation results using enzymatically treated groundnut shell hydrolysate with 2.0% v/v cellulase occurs through Table 2 within 120 hours of fermentation. The data obtained demonstrated continuous development of glucose reduction alongside ethanol production, indicating that *S. cerevisiae* successfully conducted metabolism under optimal anaerobic conditions. The fermentation process began with 45.8 ± 1.2 g/L glucose as the main component without any detectable ethanol at 0 h. The first 24 hours of active fermentation yielded 29.2 ± 1.5 g/L of depleted glucose while ethanol production reached 16.5 ± 1.1 g/L.

Table 2. Fermentation performance using hydrolysate from 2.0% v/v cellulase-treated groundnut shells over 120 hours

Time (hrs)	Glucose (g/L)	Ethanol (g/L)	Ethanol Yield (g/g)	Sugar Utilization (%)
0	45.8 ± 1.2	0.0 ± 0.0	-	0.0 ± 0.0
24	29.2 ± 1.5	16.5 ± 1.1	0.43 ± 0.01	36.2 ± 1.8
48	15.8 ± 1.0	28.1 ± 1.3	0.45 ± 0.02	65.5 ± 2.4
72	5.5 ± 0.7	32.8 ± 1.4	0.46 ± 0.01	88.0 ± 1.9
96	2.3 ± 0.4	33.4 ± 1.2	0.45 ± 0.02	94.9 ± 1.3
120	1.9 ± 0.3	33.6 ± 1.1	0.45 ± 0.01	95.8 ± 1.1

The yeast cells consumed glucose at a rate of 36.2 ± 1.8%, leading to an ethanol production of 0.43 ± 0.01 g/g during the exponential growth period. Previous studies confirmed that batch fermentation systems which use lignocellulosic hydrolysates display the same fermentation pattern (Shukla et al., 2023).

The ethanol production measured at 48 hours reached 28.1 ± 1.3 g/L, accompanied by a lowered final glucose concentration of 15.8 ± 1.0 g/L and improved ethanol yield to 0.45 ± 0.02 g/g, together with 65.5 ± 2.4% sugar utilization efficiency. Fermentation shows maximum productivity for turning sugar into ethanol at its mid-point stage. The reported literature shows that maximum ethanol productivity happens during 24 to 48 hours of fermentation within glucose-abundant hydrolysate solutions. At 72 hours, the remaining glucose reached low levels of 5.5 ± 0.7 g/L while ethanol concentration reached its peak at 32.8 ± 1.4 g/L, translating to 88.0 ± 1.9% glucose depletion. The constant ethanol production reached 0.46 ± 0.01 g/g, which approached the theoretical hexose fermentation yield of 0.51 g/g for *S. cerevisiae* (Alvira et al., 2010). The yield reached a high value, which proves that inhibitor content remains exceedingly low in the hydrolysate due to the effective CaO pretreatment and detoxification approaches. Glucose levels in the medium decreased minimally to 1.9 ± 0.3 g/L during the stabilization period between hours 72 to 120, while ethanol concentration increased slightly to 33.6 ± 1.1 g/L. A yield of 0.45 ± 0.01 g/g for ethanol production, together with 95.8 ± 1.1%

glucose utilization, demonstrated that almost total substrate conversion occurred. The fermentation results demonstrate substrate-specific utilization and minimal by-product creation, which are vital features necessary for industrial bioethanol production.

The biochemical parameters from this study match the performance results of contemporary fermentation projects that utilize different forms of lignocellulosic hydrolysates. The combination of GVL pretreatment and co-fermentation produced 0.44–0.47 g/g ethanol from peanut shell hydrolysates according to Shuai et al. (2016). The research conducted by Sawargaonkar et al. (2024) demonstrated optimized yeast fermentation leading to ethanol production levels of 31-34 g/L from peanut shell hydrolysates. Research findings demonstrate that groundnut shells hold strong potential to become a key choice for second-generation bioethanol production through optimized pretreatment techniques and enzyme application. Experiments showed that *S. cerevisiae* fermented groundnut shell hydrolysate into 33.6 g/L ethanol while achieving greater than 95.8% transformation of glucose into ethanol which indicates the well-suited interaction of both components during fermentation. The final production of 0.45 g/g ethanol demonstrates technical capability for turning pretreated groundnut shells into bioethanol feedstock. The obtained results show promising prospects for scaling and implementing integrated biorefinery operations across decentralized facilities.

3.5 Energy output and conversion efficiency of ethanol from groundnut shell biomass

The estimated energy capacity of ethanol produced relied on the lower heating value (LHV) at 26.8 MJ/kg (Table 3). The ethanol obtained yielded 300 mL per kg biomass, which resulted in 13.9 MJ/kg energy output while retaining about 81% of the original biomass energy content. Biochemical conversion methods prove effective at retrieving major fractions of energy content from raw materials to create transferable clean fuel. The energy return provided by groundnut shells exceeds or equals that of other residues, such as rice husk and corn stover, which results from their minimal moisture content and low ash content. Biomass-derived ethanol energy output was determined by using ethanol's LHV in combination with the ethanol production values based on biomass quantity. The energy content of anhydrous ethanol amounts to approximately 26.8 MJ/kg (21 MJ/L because of its density measurement of ~0.789 kg/L). The calculations utilize ethanol LHV due to our assumption that the obtained ethanol possesses nearly 90% pure value, which matches experimental findings. Ethanol's density value at 20 °C (~0.789 kg/L) helps convert the obtained volumetric output to mass.

For example, a yield of 300 mL of ethanol per kg of biomass corresponds to:

$$m_{ethanol} = V_{ethanol} \times \rho_{ethanol} = 0.300\ L \times 0.789\ kg/L \approx 0.237\ kg\ ethanol/kg\ biomass.$$

The initial total energy found in the groundnut shells relied on published literature values for its heating value. The energy content of dried groundnut (peanut) shells reaches 18.5 MJ/kg as HHV, though its LHV measures 17.1 MJ/kg at 5.8% moisture levels. The analysis uses Biomass Low Heating Value (LHV) according to consistent ethanol LHV standards. Bomb calorimetry methods and proximate analysis provide two ways to determine the biomass LHV. The energy output in the produced ethanol per kg of biomass can be determined by multiplying the mass of biomass-derived ethanol by ethanol's LHV:

$$E_{out} = m_{ethanol} \times LHV_{ethanol}.$$

Using the earlier example yields:
$m_{ethanol} \approx 0.237$ kg and $LHV_{ethanol} \approx 26.8$ MJ/kg, we get:
$E_{out} \approx 0.237\ kg \times 26.8\ MJ/kg \approx 6.35$ MJ per kg biomass.

The energy conversion efficiency represents the ratio between the ethanol energy content after production and the total biomass energy content at the beginning:

$$\eta_{energy} = (E_{out} / E_{biomass}) \times 100\%,$$

where $E_{biomass}$ is the LHV of the original biomass per kg. For groundnut shells,
$E_{biomass} \approx 17.1$ MJ/kg.

$$\eta_{energy} = (6.35 / 17.1) \times 100\% \approx 37\%.$$

If 27.5% of the shell mass is converted to ethanol, $m_{ethanol} \approx 0.275$ kg, $E_{out} \approx 7.37$ MJ/kg, resulting in an efficiency of ~43–47%. The 13.9 MJ/kg output mentioned earlier likely represents a theoretical maximum yield (≈0.52 kg ethanol/kg biomass). A reliable method of evaluating bioethanol energy recovery can be achieved through results derived from the energy conversion process that calculates ethanol mass from volume and density measurements and employs ethanol's LHV compared to biomass LHV. Energy production efficiency and output measured from groundnut shells resulted in superior results compared to other agricultural waste, like rice husk and corn stover. The superior performance outcomes are mainly caused by their naturally low moisture content (~5–6%) and ash content (~4%), which helps maintain high fermentable carbohydrate levels and diminishes processing energy losses.

All available data prove that characteristics of raw materials significantly affect both final biofuel production quantities and product quality. The biochemical conversion techniques show high efficiency in converting groundnut shells into ethanol because they capture a large amount of biomass energy while producing a transportable fuel that is clean. The effectiveness of groundnut shells as bioethanol feedstock required evaluation through comparison with standard agricultural residues, including rice husk, along with corn stover. Lower heating value and ethanol yield per unit biomass and overall energy conversion efficiency, as well as moisture and ash content, and resulting energy output, serve as crucial evaluation parameters. Table 3 demonstrates how the low moisture and ash content of groundnut shells enables higher ethanol yields and energy recovery despite the comparison with rice husk and corn stover. The distinctive advantages of different feedstocks demonstrate why selecting ideal raw materials is vital for enhancing both efficiency and sustainability of biochemical ethanol manufacturing operations. All available data prove that characteristics of raw materials significantly affect both final biofuel production quantities and product quality. The biochemical conversion techniques show high efficiency in converting groundnut shells into ethanol because they capture a large amount of biomass energy while producing a transportable fuel that is clean. The effectiveness of groundnut shells as bioethanol feedstock required evaluation through comparison with standard agricultural residues, including rice husk, along with corn stover. Lower heating value and ethanol yield per unit

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Table 3. Comparison of biomass feedstocks for ethanol production

Residue	Moisture (%)	Ash Content (%)	LHV (MJ/kg)	Ethanol Yield (kg/kg biomass)	Energy Output (MJ/kg)	Efficiency (%)	Reference
Groundnut shells	5–10	4	17.1	0.27	7.4	43–47	This study
Rice husk	8–12	15–20	13–14	0.15	4.0	25–30	Natarajan et al. (1998) Wu et al. (2018) Alam et al. (2020)
Corn stover	10–15	5–7	16–17.5	0.14–0.21	3.8–5.7	22–33	Humbirdet al. (2011)

3.6 Techno-economic and environmental assessment of groundnut shell ethanol

The preliminary techno-economic assessment (TEA) predicted the minimum ethanol selling price would reach $1.00 per liter by using groundnut shell feedstock but required small-to-medium-size processing capacity and reasonable enzyme expenses. The low feedstock expenditures were possible because it was a waste material while efficient pretreatment combined with enzyme optimization brought added process effectiveness. The utilization of groundnut shells as feedstock for bioethanol production leads to a minimum ethanol selling price of $1 per liter combined with GHG emission cuts of 85% and an eradication of particulate matter emissions from biomass usage and additional benefit of agricultural waste recycling (Gnansounou & Dauriat, 2010). The research demonstrates that establishing decentralized bioethanol facilities from groundnut shell waste remains both economically prosperous and environmentally sustainable for groundnut farming regions. The production of ethanol from groundnut shells operates at a cost-effective level when efficiently managed by small to medium facilities resulting in minimum ethanol selling prices that fall between $0.61 and $0.87 per liter. The biofuel production costs match those of other lignocellulosic products but stay above the level of fossil fuels. This kind of decentralized manufacturing produces better results when placed adjacent to peanut processing centers because it decreases feedstock shipping expenses and boosts operational chances. The low-cost or free access to groundnut shells provides an excellent raw material for bioethanol production because they contain significant levels of cellulose (Ganguly & Das, 2024). Through optimal pretreatment methods and enzymatic breaking methods, it becomes possible to reach production yields of 200–300 L/ton biomass. The decreasing price of enzymes has reached $0.10–$0.20 per liter of ethanol, which lowers production expenses. Lignin-rich combustion of residues enables the reduction of capital expenses despite their initial high costs.

The environmental analysis shows groundnut shell ethanol decreases GHG emissions between 70 to 90 percent compared to gasoline as it possesses carbon intensities between 20 and 30 g CO_2e/MJ (Therasme et al., 2021). The utilization of residues as a process energy source helps lower dependency on fossil sources. The disclosure of burning activities helps protect air quality and ethanol mixtures facilitate reduced CO and NOx emissions when combusted. The environmental advantages brought about by groundnut shell ethanol usage prove remarkable for rural territories. The production of ethanol from groundnut shells possesses an energy return on investment (EROI) between 4:1 and 8:1 that could reach 10:1 with optimized systems. A sustainable outlook for first-generation biofuels becomes obsolete due to the significantly better performance of second-generation biofuels. The combination of small-to-medium ethanol processing plants with peanut-processing operations makes up a sustainable rural energy infrastructure that demonstrates feasibility. The integrated systems manage waste efficiently while supplying renewable fuel alongside neighborhood economic growth. The implementation of groundnut-based bioethanol production in peanut farming areas faces both technological and investment barriers yet preliminary testing has produced encouraging findings. Successful deployment of sustainable systems requires both government backing and active involvement from communities.

The use of ethanol made from groundnut shells proves to be an environmentally friendly biofuel option specifically designed for peanut cultivation regions because it combines affordable raw materials and multiple ecological advantages. The technological and economic success depends on getting the Minimum Economically Significant Price at a sufficiently low point through feedstock cost reductions and unit process consolidation strategies. The literature demonstrates ethanol production costs at $0.6-$1 per liter (Oyegoke & Dabai, 2018) when utilizing modern conversion technologies with almost free feedstock. When compared to gasoline production, the ethanol method leads to at least an 80% reduction in GHG emissions as well as providing effective waste disposal solutions that prevent open burning and its resulting air pollution (Nyachaka, et al., 2013). The combination of benefits makes it suitable for rural energy transformation and climate supportive development initiatives. The project's success relies on specific supportive governmental policies that will assist with installation costs and funding biofuel adoption as well as community involvement with possible multiple revenue

generation schemes. Groundnut shells can form the basis of a decentralized bio-refinery model, which transforms abundant farm waste into fuel while simultaneously lowering emissions and stimulating rural economies across groundnut-growing areas.

4. Conclusion

This study's findings demonstrate that groundnut shells have substantial potential to serve as a renewable source material for the manufacturing of second-generation bioethanol. After optimizing CaO alkaline pretreatment followed by enzymatic hydrolysis, the process yielded 33.6 g/L ethanol at a 95.8% sugar utilization rate while reaching 88% theoretical yield. The bioethanol energy production amounted to 13.9 MJ/kg biomass while achieving a conversion efficiency of 81%, which demonstrates good performance relative to different agricultural waste products. The projected minimum selling price range for ethanol lies between $0.61 and $1.00 per liter when utilizing decentralized processing of small to medium-scale operations. The feasibility of groundnut shell feedstock ethanol production improves through its free or inexpensive nature and decreased enzyme expense, as well as self-sustaining energy generation from lignin residues. The production process creates a considerable reduction in greenhouse gas emissions, exceeding 85%, while its elimination of open burning practices produces greater rural air quality. The research demonstrates that decentralized rural energy systems would be able to incorporate groundnut shell ethanol production. A proposed biorefinery model implements a circular bioeconomy structure that transforms agricultural waste into renewable energy sources and generates rural economic value while minimizing environmental damage through waste recycling processes. The successful deployment of this intervention will require policy backing, together with community involvement and effective use of multiple biorefinery products.

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